# Measurement of Dilute Mixture Vapor-Liquid Equilibrium Data for Methanol-Water and Ethanol-Water Mixtures with a Recirculating Still

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Keywords: activity coefficient, dilute mixture, experimental method, vapor-liquid equilibria

#### **Abstract**

A Gillespie-type still which recirculates vapor and liquid phases was used in the measurement of pressure and phase compositions for dilute aqueous solutions of methanol and ethanol at vapor-liquid equilibrium at temperatures between 50 and 100 °C. Liquid and condensed vapor samples from each run were analyzed for alcohol concentration by gas chromatography. Liquid activity coefficients calculated with the experimental data are compared with infinite dilution activity coefficients reported in the literature.

The measured infinite dilution activity coefficients agree within 5% with independent measurements at the lower temperatures and are well represented by curves with slopes that agree with experimental enthalpy of mixing data. The curves, when extrapolated to lower temperatures, agree within 8.5 and 5.5%, respectively, of the mean values of numerous measurements for aqueous solutions of methanol and ethanol.

#### Introduction

Activity coefficients are measures of the deviation from ideal distribution of components between equilibrium phases. Limiting values of activity coefficients (at infinite dilution) are useful in calculating phase concentrations for dilute mixtures and in correlating phase equilibrium models [1]. Several experimental methods have been used to measure activity coefficients at infinite dilution including gas chromatography, ebulliometry, and static pressure measurements [2]. A technique which has rarely been used for dilute mixtures [3,4] is that of analysis of vapor and liquid phases sampled from a recirculating still. Sampling from a recirculating still provides a simple, direct experimental technique to measure vapor-liquid equilibrium data for dilute mixtures given an accurate method of analysis of the liquid and condensed vapor samples.

This work demonstrates the feasibility of using a recirculating still in the measurement of equilibrium pressure, temperature, and liquid and vapor phase compositions of dilute mixtures. The water-methanol and water-ethanol systems are exceptional test systems because of existing infinite dilution activity coefficient data over the temperature range of applicability of still measurements (50 to 100 °C), existing measurements of enthalpy of mixing, and the large number of measurements of infinite dilution activity coefficients at 25 °C for both systems.

## **Experiments**

#### Materials

Water (Sigma-Aldrich HPLC grade), methanol (J. T. Baker, 100.0% assay), and ethanol (Union Carbide, 200 proof) were used in the still experiments; 2-methyl-2-propanol (Sigma-Aldrich HPLC grade, 99.5% assay) was used as an internal standard in the gas chromatography analysis. Each of the chemicals was used as received.

# Experimental Equipment and Procedures

Pressure-temperature-liquid and vapor composition (PTxy) data were obtained from experiments made with a Gillespie-type glass recirculating still [5]. A schematic of the experimental equipment is given in Figure 1. The boiler is heated electrically by a resistance heater. A vapor-lift pump sprays vapor and liquid slugs on the thermometer well in the vapor and liquid disengagement chamber where the two phases are separated. Liquid and condensed vapor are collected in sampling cells which overflow into the boiler. The still is connected to a manostat through a standard condenser which is cooled with a propylene glycol-water mixture. The entire apparatus is insulated except the condensers and the vapor and liquid sample cells.

The pressure is controlled by a Wallace and Tiernan manostat and is measured by a pressure transducer to within 1 torr. Temperature is measured with a Hart model 1506 thermometer with a Hart model 5614 platinum resistance probe. Reported temperatures are accurate to  $\pm$  0.1 °C. Vapor and liquid compositions are measured with the flame ionization

detector (FID) of a Hewlett-Packard gas chromatograph (Model 5890 Series II equipped with a 60 m J&W Scientific DB-1 capillary column). An internal standard of 1000 ppm 2-methyl-2-propanol is added to all samples and peak areas relative to the standard are measured. The FID was calibrated with mixtures of known composition, prepared gravimetrically, over the composition range 10 - 2000 ppm alcohol. The composition measurements are averages of three chromatographic injections; the standard deviation is less than 2% of the mean for vapor samples and less than 3% of the mean for liquid samples.

The experimental procedure is as follows. Approximately 170 ml of a gravimetrically-prepared, 250 ppm alcohol in water solution is poured into the boiler through the vertical condenser. The still is then connected to the manostat and the desired pressure is set. The electrical heater is turned on and adjusted to obtain steady boiling of the solution. Steady boiling is maintained at constant pressure for three to four hours after which the heater is turned off, pressure is raised to atmospheric, and 10-20 ml samples of liquid and condensed vapor are taken from the sample cells for gas chromatographic analysis.

# Calculation of Activity Coefficients

The liquid phase activity coefficients of the alcohol at equilibrium were calculated by equating the fugacities of the liquid and vapor phases:

$$f_2^{(L)} = f_2^{(V)} \tag{1}$$

Expressing the liquid fugacity in terms of an activity coefficient and the vapor fugacity in terms of a fugacity coefficient gives:

$$f_2^{(L)} = \gamma_2 x_2 f_2^{\circ} \tag{2}$$

$$\mathbf{f}_{2}^{(V)} = \phi_{2} \mathbf{y}_{2} \mathbf{P} \tag{3}$$

Substitution of equations 2 and 3 into equation 1 and rearrangement gives:

$$\gamma_2 = \frac{\phi_2 y_2 P}{x_2 f_2^{\circ}} \tag{4}$$

Equation 4 was used to calculate activity coefficients from the experimental data. For a standard state of pure liquid at system P and T, the liquid standard state fugacity  $f_2^{\circ}$ , after assumption of liquid incompressibility, is given by [6]:

$$f_{2}^{\circ} = P_{2}^{\text{sat}} \phi_{2}^{\text{sat}} \exp \left( \frac{v_{2}^{\text{sat(L)}} (P - P_{2}^{\text{sat}})}{RT} \right)$$
 (5)

where the exponential term is the Poynting correction. The Antoine equation,

$$\log_{10} P_{i}^{\text{sat}} = A_{i} - \frac{B_{i}}{t + C_{i}}$$
 (6)

was used to calculate vapor pressure values for the pure alcohols. The saturated liquid molar volume was calculated with the following equation:

$$v_i^{\text{sat(L)}} = va_i + vb_i(T) + vc_i(T)^2$$
 (7)

Vapor pressure and molar volume data from 10 to 110 °C obtained from DIPPR [7] were fitted with equations 6 and 7, respectively; the fitted constants are given in Tables 1 and 2. The fugacity coefficients were determined with the pressure explicit virial equation truncated to the first correction term,

$$\frac{PV}{RT} = 1 + \frac{B_m P}{RT} \tag{8}$$

where

$$B_{m} = y_{1}^{2}B_{11} + 2y_{1}y_{2}B_{12} + y_{2}^{2}B_{22}$$

$$\tag{9}$$

The relationship:

$$\ln \phi_2 = \frac{1}{RT} \int_0^P \left[ \left( \frac{\partial V}{\partial n_2} \right)_{T,P,n_1} - \frac{RT}{P} \right] dP$$
 (10)

gives:

$$\ln \phi_2 = \left(2y_2 B_{22} + 2y_1 B_{12} - B_m\right) \frac{P}{RT}$$
 (11)

The correlation of Hayden and O'Connell [8] was used to obtain the cross-coefficient  $B_{12}$  for the binary systems and the second virial coefficient for each of the pure components. The values of critical temperature, critical pressure, dipole moment, and radius of gyration are used in the Hayden and O'Connell correlation; these were obtained from DIPPR [7] and are given in Table 3. The association and solvation parameters used in the Hayden-O'Connell correlation are given in Table 4. The reported activity coefficients are estimated to be accurate to  $\pm$  5%.

# Experimental Results

Pressure-temperature-liquid and vapor composition (PTxy) measurements were made for dilute, binary, mixtures of water with methanol and ethanol at temperatures between 50 and 100 °C. The measured temperature, pressure and equilibrium mole fractions are given for each mixture of the experimental study in Table 5. The calculated infinite dilution activity coefficient values are given in Table 5 and are compared with literature data in Figures 2 and 3.

The infinite dilution activity coefficient for methanol at 59.9 °C obtained with the recirculating still, 2.15, is almost identical to the 2.13 value at 60 °C measured by Hofstee et al. [13] with gas chromatography. The value obtained with the recirculating still at 99.4 °C, 2.57, is 13% greater than the 2.28 value of Grafahrend [17] at 100.2 °C measured with ebulliometry. Poorer agreement is found with the ebulliometric data of Bergmann and Eckert [12]; interpolated values from the recirculating still data are more than 30% higher than the three measurements of Bergmann and Eckert within the temperature range of the present study. The data of Bergmann and Eckert are also significantly lower than the value of Lee [24] at 55 °C and, when extrapolated to lower temperatures, the data of Hofstee et al. [13] at 40 °C, Pividal, et al. [9] at 20, 30, and 40 °C, Christian et al. [10] at 25 and 35 °C, and all eleven other available measurements at 25 °C.

The infinite dilution activity coefficient data for ethanol obtained with the recirculating still can be directly compared with six measurements by other researchers. The measured data (or an interpolated value) are within 5% of values reported by Pemberton and Mash [30], Lee [24], and Pividal et al. [9] at 50, 55, and 60 °C, and within 10% of values reported by Pemberton and Mash and Grafahrend [17] at 70 and 100 °C, respectively. The values given by Pemberton and Mash were obtained by graphical extrapolation of activity coefficient data obtained by dilute total pressure measurements; the value given by Lee is from a dilutor technique; the data of Pividal et al. are from static pressure measurements. The one comparison that differs by more than 10% is that at 90 °C where the value reported in this study is 15% greater than that reported by Pemberton and Mash.

The curves in Figures 2 and 3 were obtained by fitting the measured infinite dilution activity coefficient data to equations which give slopes of activity coefficient versus temperature which match experimental enthalpy of mixing data according to the following relationship [33]:

$$\left[\frac{\partial \ln \gamma_2^{\infty}}{\partial (1/T)}\right]_{P_x} = \frac{h_2^{E\infty}}{R}$$
 (12)

where  $h_2^{E\infty}$  is the partial molar excess enthalpy of mixing at infinite dilution. Values of  $h_2^{E\infty}$  data were obtained from the initial slope at  $x_2 = 0$  of water (1) - methanol (2) enthalpy of mixing data measured by Battler and Rowley [34] at temperatures between 20 and 50 °C and from the infinite dilution enthalpy of mixing data of Pemberton and Mash [30] for ethanol-water mixtures between 25 and 90 °C. Plots of  $h_2^{E\infty}$  / R versus 1/T for the water (1) - methanol (2) and water (1) - ethanol (2) systems are given in Figure 4; these data were fitted with the lines shown in the figures. The linear equations were integrated and integration constants were obtained by fitting to the infinite dilution activity coefficient data

of this study. The final equations which represent the data and give the correct slopes are for water (1) - methanol (2):

$$\ln \gamma_2^{\infty} = -0.2626 + 1205 \left(\frac{1}{T}\right) - 283740 \left(\frac{1}{T}\right)^2 \tag{13}$$

and for water (1) - ethanol (2):

$$\ln \gamma_2^{\infty} = -3.4792 + 4193.4 \left(\frac{1}{T}\right) - 817800 \left(\frac{1}{T}\right)^2 \tag{14}$$

Extrapolation of equations 13 and 14 to 25 °C gives values of  $\gamma_2^\infty$  equal to 1.80 and 4.00 for aqueous methanol and ethanol systems, respectively. The extrapolated value for the water-methanol system is within the range of twelve independent experimental measurements of  $\gamma_2^\infty$  and is within 8.5% of 1.66, the average of the literature values. The extrapolated value for the water-ethanol system is within the range of ten independent experimental measurements of  $\gamma_2^\infty$  and is within 5.5% of their average, 3.80.

#### **Conclusion**

Gas chromatographic analysis of samples from a recirculating still provided a simple, direct method of measurement of vapor and liquid compositions at equilibrium for dilute aqueous solutions of methanol and ethanol. Infinite dilution activity coefficients calculated from the experimental data compare favorably with some independent measurements and are consistent with measured enthalpy of mixing measurements and the consensus of  $\gamma_2^{\infty}$  at 25 °C.

#### **Nomenclature**

 $\begin{array}{lll} A_i,\,B_i,\,C_i & \quad & \text{Antoine vapor pressure equation constants} \\ B & \quad & \text{second virial coefficient} \\ f & \quad & \text{fugacity} \\ h & \quad & \text{partial molar enthalpy} \\ n & \quad & \text{number of moles} \end{array}$ 

P pressure R gas constant t temperature, °C T absolute temperature, K

v molar volume

V volume

va<sub>i</sub>, vb<sub>i</sub>, vc<sub>i</sub> molar volume equation constants

x liquid mole fraction y vapor mole fraction

#### Greek Letters

φ vapor-phase fugacity coefficient

γ liquid-phase activity coefficient standard state: pure liquid at system T and P

# **Subscripts**

1 of component 1 2 of component 2 i of component i m of the mixture

## **Superscripts**

E excess L liquid phase

sat saturation conditions of pure component

V vapor phase
° standard state
∞ at infinite dilution

## Acknowledgment

Keith Gayle performed the still experiments and the gas chromatographic analyses.

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 Table 1:
 Antoine Equation Constants\*

Component, i	$A_i$	$B_i$	Ci
Methanol	7.948839	1501.485	231.785
Ethanol	8.046684	1563.590	224.363

<sup>\*</sup>Antoine equation:  $\log_{10} P_i^{\text{sat}} = A_i - B_i/(t + C_i)$ ;  $P_i^{\text{sat}}$  in torr, t in °C.

 Table 2:
 Molar Volume Equation Constants\*

Component, i	vai	vbi	vci
Methanol	41.376	-0.053417	0.0001701
Ethanol	59.278	-0.069692	0.0002262

<sup>\*</sup>Molar volume equation:  $vol = va_i + vb_i*T + vc_i*T^2$ ; vol in cm<sup>3</sup>/mole, T in K.

**Table 3:** Pure-Component Properties Used in Calculations of Equilibrium Pressure and Vapor Composition\*

Component	Critical Temperature (°C)	Critical Pressure (atm)	Dipole Moment ((J-m <sup>3</sup> ) <sup>0.5</sup> x 10 <sup>25</sup> )	Radius of Gyration (m x 10 <sup>10</sup> )
Methanol	239.5	79.93	5.376	1.552
Ethanol	240.8	60.69	5.347	2.259
Water	374.0	217.67	5.850	61.50

<sup>\*</sup>Values are from DIPPR [7].

**Table 4:** Hayden-O'Connell Association and Solvation Parameters Used in Calculations of Equilibrium Pressure and Vapor Composition

System	$\eta_{11}$	$\eta_{22}$	$\eta_{12}$	
Water (1) - Methanol (2)	1.70	1.63	1.55	
Water (1) - Ethanol (2)	1.70	1.40	1.55	

 Table 5:
 Measured PTxy Data and Infinite Dilution Activity Coefficients

P (torr)	T (°C)	$X_2$	<b>y</b> <sub>2</sub>	$\gamma_2^{\infty}$
Water (1) - Methan	nol (2)			
150	59.9	5.089 x 10 <sup>-5</sup>	4.459 x 10 <sup>-4</sup>	2.15
228	69.2	4.498 x 10 <sup>-5</sup>	3.975 x 10 <sup>-4</sup>	2.30
357	79.9	$5.132 \times 10^{-5}$	$4.526 \times 10^{-4}$	2.44
526	89.8	$4.501 \times 10^{-5}$	$3.805 \times 10^{-4}$	2.47
749	99.4	6.251 x 10 <sup>-5</sup>	5.237 x 10 <sup>-4</sup>	2.57
Water (1) - Ethano	1 (2)			
88	48.9	1.947 x 10 <sup>-5</sup>	2.423 x 10 <sup>-4</sup>	5.24
151	60.1	$2.061 \times 10^{-5}$	$2.747 \times 10^{-4}$	5.75
236	70.0	$2.686 \times 10^{-5}$	$3.717 \times 10^{-4}$	6.12
357	79.9	$2.305 \times 10^{-5}$	$3.125 \times 10^{-4}$	6.13
526	89.7	$2.395 \times 10^{-5}$	$3.470 \times 10^{-4}$	6.71
742	99.1	$2.408 \times 10^{-5}$	$3.241 \times 10^{-4}$	6.34

# **Figure Captions**

- Figure 1: Schematic Diagram of Recirculating Still.
- **Figure 2:** Infinite Dilution Activity Coefficients for the Water (1) Methanol (2) System.
- **Figure 3:** Infinite Dilution Activity Coefficients for the Water (1) Ethanol (2) System.
- **Figure 4:** Partial Molar Excess Enthalpy at Infinite Dilution for the Water (1) Methanol (2) and Water (1) Ethanol (2) Systems.

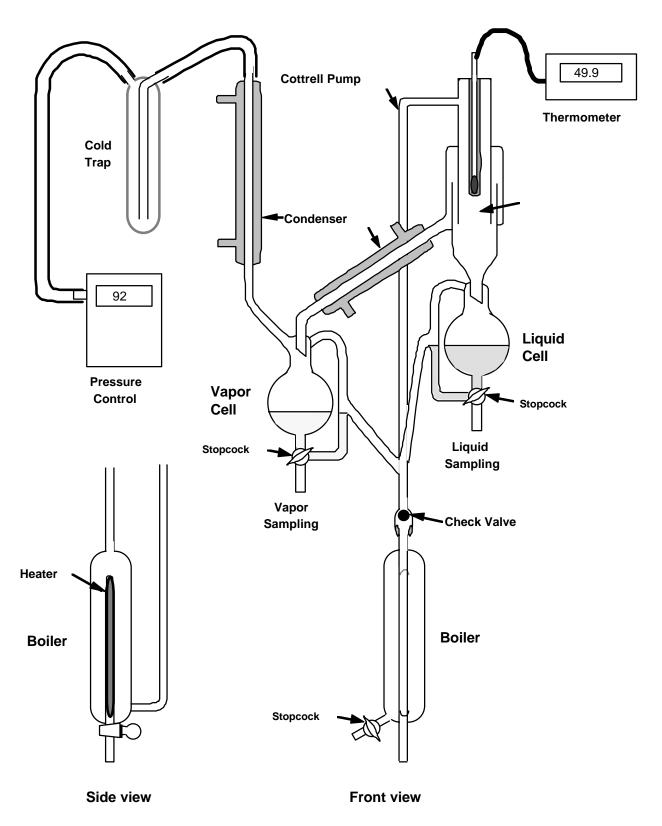
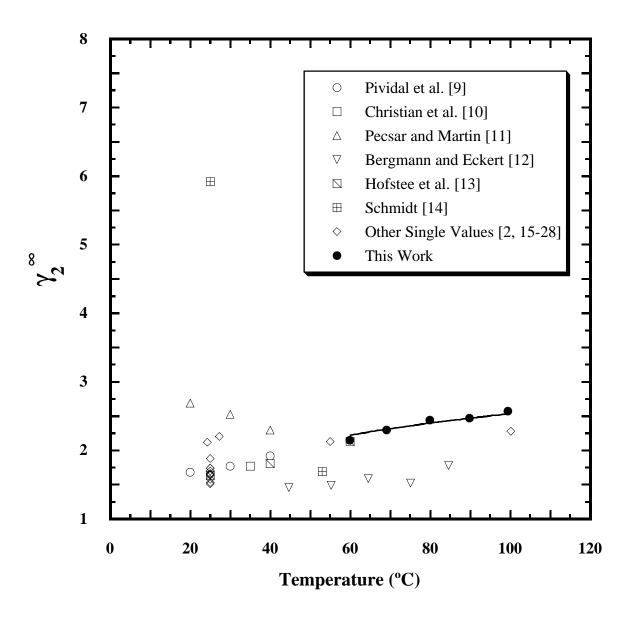
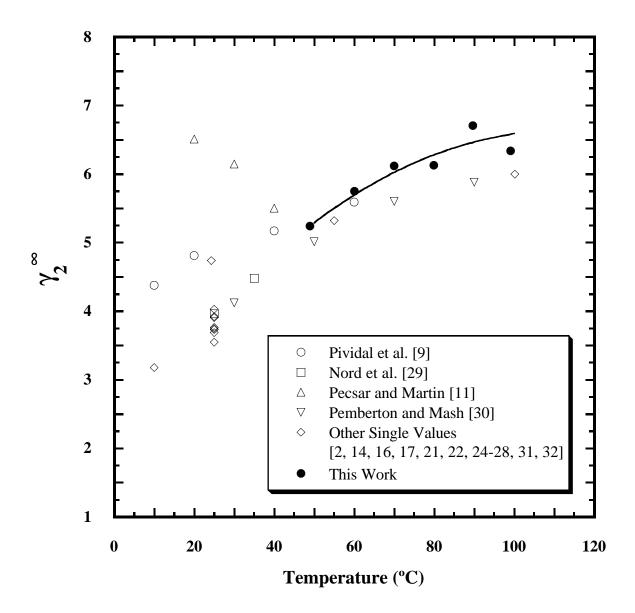


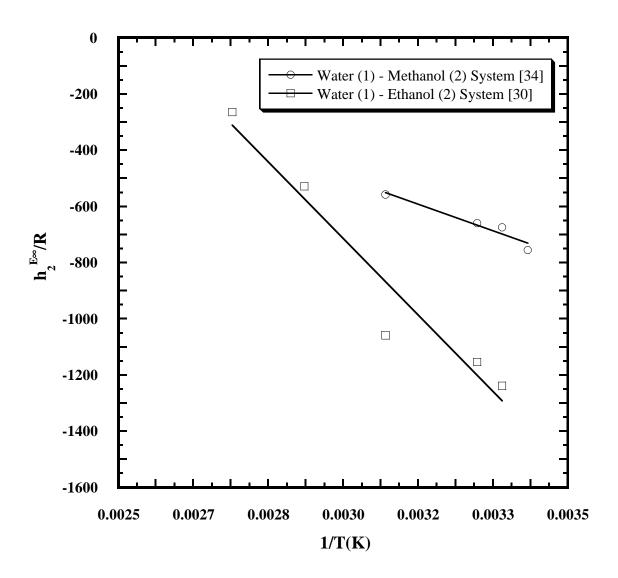
Figure 1: Schematic Diagram of Recirculating Still.



**Figure 2:** Infinite Dilution Activity Coefficients for the Water (1) - Methanol (2) System.



**Figure 3:** Infinite Dilution Activity Coefficients for the Water (1) - Ethanol (2) System.



**Figure 4:** Partial Molar Excess Enthalpy at Infinite Dilution for the Water (1) - Methanol (2) and Water (1) - Ethanol (2) Systems.